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# COMPUTER SIMULATIONS OF EPOXY ADHESIVE MONOMER INTERACTIONS WITH ALUMINA SURFACES

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POLYMER RESEARCH BRANCH

August 1992



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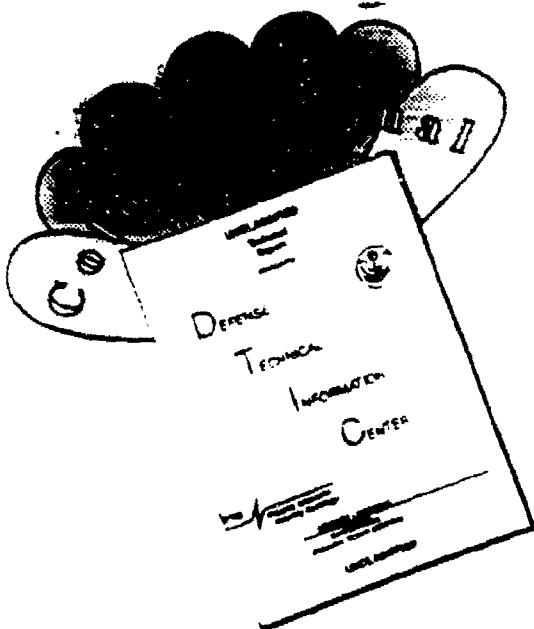
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**ABSTRACT**

An ongoing program in our laboratory seeks to elucidate the effect of aluminum oxide on the cure chemistry of epoxy adhesives. The project includes the use of molecular dynamics (MD) techniques to carry out real time simulations of the interaction of various epoxy adhesive monomers with idealized alumina surfaces. Adhesive monomers investigated include the diglycidyl ether of bisphenol A (DGEBA), a brominated form of DGEBA, diaminodiphenyl sulfone (DDS) and methylene dianiline (MDA). Both crystalline and amorphous forms of alumina at different levels of hydration have been simulated. The simulations illustrate the preferred orientations of the organic molecules with respect to the alumina surfaces and suggest which functional groups are most influential in determining this orientation. The model and experimental systems correlate well, showing similar response to changes in organic molecular structure, alumina morphology, and level of hydration. Model studies of this type can aid the understanding of the critical interphase region of adhesive bonds, including factors which affect bond durability, and have the potential to be used in the design of improved adhesives.

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## CONTENTS

	Page
INTRODUCTION .....	1
EXPERIMENTAL .....	2
RESULTS .....	3
CONCLUSIONS .....	6

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## INTRODUCTION

The interaction between the aluminum oxide layer on the surface of aluminum metal and the chemical components of an adhesive system is critical to the performance of adhesive bonds to aluminum. The U.S. Army Materials Technology Laboratory (MTL) is conducting an investigation into the effects of alumina on the cure chemistry of epoxy adhesives. It has been determined that some forms of alumina are capable of catalyzing epoxy homopolymerization in the absence of any other catalyst or curing agent.<sup>1</sup> Other experiments are in progress to study the structure and composition of species chemisorbed on or bonded to alumina particles (used as model surfaces) which have been exposed to epoxy adhesive systems. In an effort to shed light on the nature of the interaction of epoxy adhesives with alumina, molecular dynamics (MD) simulations have been carried out on constructs of epoxy monomers and aluminum oxide lattices. The goal of these computational studies is to determine if the behavior of the modeled systems can be correlated to the results of the experimental program. If successful, the models may facilitate the rational design of epoxy resin components with tailored affinities for various surfaces, will help guide future research into the nature of the interphase, and could lead to the development of theoretical methods to predict the service life of adhesively bonded structures.

The molecular dynamics technique utilizes what is essentially a mechanical model of the molecules under study. Atoms are represented as solid spheres with characteristic masses and radii. Bonds, specific to the atom types they connect, are represented by springs with a linear elastic constant and a nominal equilibrium (zero applied force) length. Factors affecting molecular motion such as temperature, electrostatic charges, and Van der Waal's forces can be included in the dynamics calculations. The parameter set or "force field" (atomic masses, bond lengths, bond angles, bond stretching energies, etc.) upon which the model is based is derived from experimental data such as X-ray crystal structure determinations and vibrational spectra. In the ideal case, the optimized (lowest energy) geometry of a molecule calculated using the force field will match the experimentally determined equilibrium structure. In order to improve the accuracy of the computational results, there are usually several atom types defined in the force field for each chemical element to be modeled. For example, aromatic and aliphatic carbon would be defined as separate atom types with different parameters. There are a rather limited number of force fields in general use, perhaps the most popular being the MM2 force field developed by Allinger and co-workers<sup>2a,2b</sup> for small molecules. The commercially developed Tripos force field,<sup>3</sup> used in these calculations, and the AMBER force field,<sup>4</sup> optimized for biomolecules are other examples. These parameter sets have been developed and refined over several years and the results obtained using them are usually in quite good agreement with experiment.

The simulation of real time molecular motion is carried out by integrating Newton's laws of motion over time for the masses in the system after initial velocity is imparted to them (typically by using a random number algorithm). Molecular dynamics simulations have been used to successfully simulate real time physical phenomena in several different systems.

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Examples include simulating the rheological properties of polymers,<sup>5</sup> ion transport processes,<sup>6</sup> gaseous diffusion in polymers,<sup>7</sup> and surface effects in micellar systems.<sup>8</sup> The principal limitation of the MD technique is that it is computationally intensive, since the time step over which integration is performed must be very small (on the order of one femtosecond (fs)) in order to avoid unrealistically large molecular motions. The length of simulated events is typically restricted to nanoseconds using the fastest computers currently available. Given the success of the method to date and the rapid advances being made in computer performance, it is likely that the number of reported MD applications will continue to grow.

## EXPERIMENTAL

Molecular dynamics simulations were carried out using Sybyl™ molecular modeling software<sup>9</sup> on a Digital Equipment Corporation microVAX™ cluster. The Tripos force field was employed in the simulations.<sup>3</sup> Simulations were generally carried out at a constant temperature of 300 K. The contributions of electrostatic forces were included in the calculations. Partial atomic charges for the organic molecules were determined using the well known MNDO program.<sup>10a,10b</sup> Formal charges of +3 and -2 were assigned to the aluminum and oxygen atoms, respectively, of the alumina constructs. Published values of aluminum (+3) and oxygen (-2) crystal ionic radii were used in the constructs.<sup>11</sup> Alumina crystal structure parameters were obtained from the literature.<sup>12,13</sup> The amorphous alumina structure used in the simulations was created as follows: Unit cells of corundum ( $\alpha$ -alumina) in random orientations were packed into a box using an algorithm provided in Sybyl™. The density of alumina in the box was set to 3.2 g/cc, an average value for chromatography grade amorphous alumina which was used in laboratory experiments. The constraints on the atomic positions were removed, electrostatics turned off, and the Sybyl™ minimizer allowed to act on the system until it achieved an amorphous appearance. A check of interatomic distances in the resulting structure showed no contacts closer than those in corundum. Water was incorporated into the amorphous alumina model by randomly placing water molecules in close proximity to the alumina surface, then equilibrating the system with a one picosecond (ps) dynamics run. In a typical simulation, four molecules of an epoxy resin component, such as the diglycidyl ether of bisphenol A (DGEBA), were arrayed at random over a segment; e.g., 30 Å x 30 Å x 10 Å, of an alumina fragment. The starting positions of the organic molecules were typically 5 Å to 10 Å from the alumina surface and from each other. The positions of atoms in the alumina structure were held constant throughout the simulation. The organic molecules (and water molecules, when present) were then allowed to move without constraint until an equilibrium condition was established, as evidenced by the calculated system energy reaching a stable minimum value. This typically required between 5 ps and 30 ps of real time simulations. The time step between conformations was 1 fs, so a typical calculation would produce 5000 to 30,000 conformations. Conformations were recorded every 25 fs. Simulations typically required 40 to 90 hours of CPU time on a microVAX™ 3800 computer.

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## RESULTS

Dynamics simulations were used for this study rather than single point energy minimizations to overcome the tendency for such static minimizations to become trapped in a local minimum on the conformational potential energy surface of the system. Although the dynamics calculations are rather computationally intensive for systems of the size studied here (1000 to 3000 atoms), they are the most effective way of achieving a global minimum energy conformation. The dynamics simulations also generate a large amount of data which may be used to establish relationships between the model and experimental observations. Among these are energies of interaction between the organic and inorganic components of the system, the bond lengths and angles for the unconstrained organic molecules as a function of time, and the visual representations of the structures which directly illustrate the preferred conformation of the organic molecules with respect to the alumina surface. In addition, instantaneous values for system potential energy, kinetic energy, and local effective temperature are determined.

Two epoxy monomers and two aromatic amine curing agents have been studied. The epoxies are DGEBA and 3,3',5,5'tetrabromo DGEBA (DGEBA-Br). The curing agents are 4,4'-diaminodiphenylsulfone (DDS) and methylene dianiline (MDA). Two forms of alumina were studied in an attempt to correlate the effects of alumina morphology on experimental and simulated results. The alumina structures used in simulations were corundum ( $\alpha$ -alumina) and an amorphous  $\text{Al}_2\text{O}_3$  structure prepared as previously described. Water was added to the amorphous structure to simulate aluminas with 3% and 7.5% by weight adsorbed water. Figures 1 through 4 illustrate the appearance of the surfaces presented to the organic molecules by each of the alumina constructs.

Before considering the results of the simulations, it is necessary to review the following condensed results of MTL's experimental studies of the effects of alumina on epoxy resin cure chemistry. Differential scanning calorimetry (DSC) studies of mixtures of DGEBA and particulate alumina (chromatography grade, neutral, activity I) have shown that amorphous alumina catalyzes the homopolymerization of the epoxies.<sup>1</sup> DSC studies of mixtures of alumina with DGEBA and DDS show that amorphous alumina also accelerates the rate of the epoxy-amine reaction. Corundum, however, was found to be completely inert under the same conditions.<sup>1</sup> Addition of water to the amorphous alumina systems has different effects on homopolymerization and amine cure. Addition of water apparently inhibits epoxy homopolymerization in the presence of alumina, based on the shift of the DSC peak exotherm (Figure 5), but enhances the acceleration of the epoxy-amine reaction (Figure 6). DSC results also suggest that DGEBA-Br is less susceptible to homopolymerization in the presence of alumina than DGEBA (Figure 7).<sup>14</sup>

The simplest analysis of the simulations is accomplished by visually examining the structures that result. As might be anticipated, the polar functional groups on the organic molecules are the principal sites of interaction between the organic molecules and the alumina surfaces in the models. Thus, the oxirane oxygens on the DGEBA molecules are the primary site of interaction, followed by the ether oxygens linking the epoxy groups to the phenyl rings (Figure 8). Interestingly, the bromine sites on the DGEBA-Br molecule appear to be indifferent to or even repelled to some extent by the alumina surfaces (Figure 9). In the case of MDA, the amine nitrogens are the sole sites of observed binding activity (Figure 10). In simulations of DDS, both the sulfone group and the amine groups are seen

14. ZUKAS, W. X. Unpublished results. U.S. Army Materials Technology Laboratory.

to interact with the alumina surfaces. The most common end state conformation for DDS on amorphous alumina was that which places the sulfone group and one amine group in close proximity to the surface with the intervening phenyl ring lying flat on the surface (Figure 11). This predicted orientation is unanticipated and has not been confirmed by experiment. On corundum, the sulfone group was almost exclusively the site of interaction between DDS and the surface (Figure 12), a preliminary indicator of the reduced activity of the corundum surface compared to the amorphous surface. In systems incorporating water, the organic molecules appear to avoid water sites as they interact with the surface suggesting that the presence of water interferes with adhesive component binding to alumina.

One of the principal quantitative results of these simulations is a calculated binding energy or surface affinity for the various combinations of organic molecules on inorganic surfaces. Surface affinity values were determined by performing single point energy calculations on several structures at the equilibrium state, subtracting out all contributions to the system energy not due to organic-inorganic interactions, and averaging the results. Although these results are reported as kilocalorie values, it is not clear that the absolute magnitude of these results, as determined by the algorithm used, is meaningful. As such, the numbers reported are best considered only as relative arbitrary affinity values, the largest negative value indicating the greatest affinity. These results are presented in Table 1. Calculated binding energies for DDS on amorphous alumina are higher than those of any of the other systems studied. This observation compares favorably to the result of simple column chromatography experiments in which DDS is preferentially retained by an alumina stationary phase, relative to other adhesive components studied. Comparing the forms of epoxy monomer, DGEBA shows a greater affinity for alumina than DGEBA-Br (Table 1). This result correlates well with the experimental observation of reduced reactivity toward homopolymerization for the brominated resin in the presence of alumina. As water is added to the systems containing amorphous alumina, the affinity of organic molecules for the surface decrease in all cases. This trend parallels the experimental finding that adding water retards the alumina-catalyzed homopolymerization reaction but does not coincide with the observed increase in reaction rate for epoxy-amine systems as water is added. This apparent inconsistency may be explained by the reported catalytic effect of added hydroxyl groups or proton donors on the epoxy-amine reactions, independent of the alumina surface.<sup>15</sup>

Table 1. CALCULATED AFFINITIES OF ADHESIVE MONOMERS FOR ALUMINA SURFACES (KCAL)

	Corundum	Amorphous	Amorphous +3% H <sub>2</sub> O	Amorphous +7.5% H <sub>2</sub> O
DGEBA	-848	-1187	-1158	-665
DGEBA-Br	-533	-1055	-718	-673
DDS	-2327	-2714	-2511	-2352
MDA	-560	-723	-612	-382

The relative strength of the interactions of alumina with various atoms in the organic molecules can also be probed by looking at how bonds involving these atoms are affected by approach to the surface. In every case, critical bond lengths in the functional groups of the

15. SHECHTER, L., WYNSTRA, J., and KURKJY, R. P. *Ind. and Engr. Chem.* v. 48, 1956, p. 94.

organic molecules were perturbed as the molecules approached the alumina surfaces. By the same token, other bonds in the molecules, such as the C-H bonds in DGEBA, were unaffected. These results were quantified by comparing the equilibrium length of selected bonds (no alumina present) to their length while interacting with the surface (Table 2). In the case of C-O bonds in the oxirane ring of the epoxy molecules, approaching the alumina surface causes an increase in the median bond length as well as in the vibrational amplitude of the bond. This suggests a reduction in the C-O bond order and an enhanced reactivity of the epoxy group, and may be related to the observed catalytic activity of alumina toward epoxy homopolymerization.<sup>1</sup> In general, the trends observed in the bond length calculations for the epoxies are the same as those witnessed in the surface affinity calculations and they support the same correlations to experimental results. The deviations from the affinity trends in the values found for the sulfone S=O bond of DDS are unexplained. It should be noted, however, that the standard deviation of the mean S=O bond perturbations were so large (as much as 39% in the worst case) that the values may be considered invariant for practical purposes. The only conclusion to be drawn is that the model predicts a major role for the sulfone group in the interaction of DDS with alumina. This prediction may be at odds with the observation that sulfone-containing mono-amines are not incorporated into species bonded to the surface of alumina particles in model compound studies.<sup>1</sup> This apparent discrepancy is the subject of continuing investigation. The behavior of the N-H bonds of the amine groups of DDS and MDA conforms more nearly to the trends of the affinity calculations for these molecules. As with the affinity calculations, no obvious correlation can be drawn between the calculated effect on N-H bond lengths and the experimental observations.

Table 2. PERCENT CHANGE IN MEDIAN BOND LENGTHS DUE TO INTERACTION WITH SURFACE

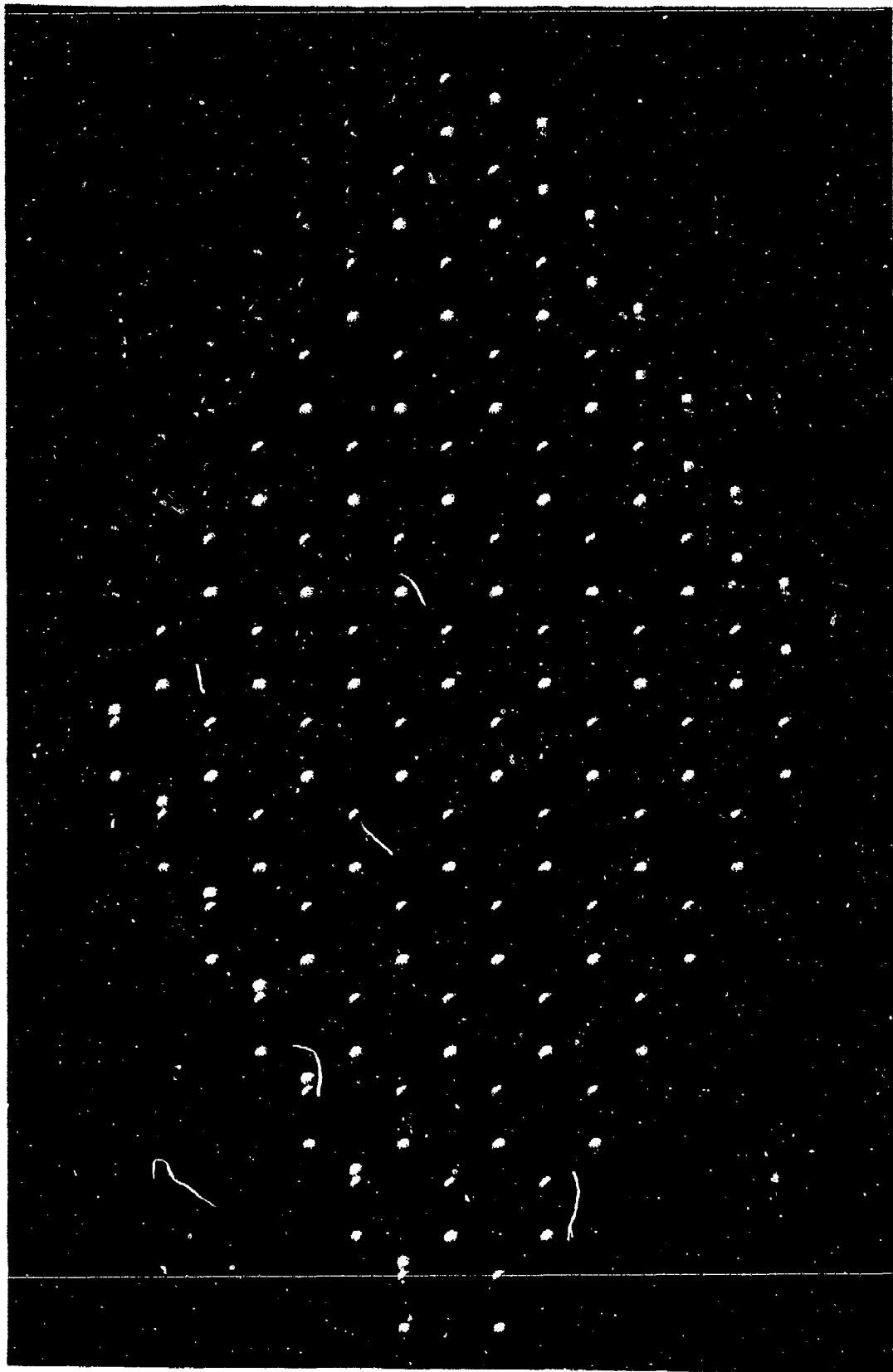
	Corundum	Amorphous	Amorphous +3% H <sub>2</sub> O	Amorphous +7.5% H <sub>2</sub> O
Oxirane C-O DGEBA	2.5	5.7	4.7	2.4
Oxirane C-O DGEBA-Br	2.1	4.7	2.5	2.1
Amine N-H DDS	5.6	4.7	3.7	4.7
Sulfone S=O DDS	16.3	13.8	17.1	15.2
Amine N-H MDA	4.6	4.6	6.5	2.8

Two forms of alumina were used in the simulations in order to determine to what extent alumina morphology affects the results. Corundum or  $\alpha$ -alumina is the densest and most stable form of alumina. The alumina layer on an actual metal surface prepared for bonding is typically amorphous or polymorphic and was represented in the simulations by the amorphous Al<sub>2</sub>O<sub>3</sub> construct described previously. Both binding energy calculations and bond length analyses show that all of the organic species interact more strongly with the amorphous form of alumina than with corundum (Tables 1 and 2). This observation correlates with the experimental result that alumina morphology critically affects its activity with respect to epoxy homopolymerization and epoxy-amine reactions, with amorphous alumina being more active than corundum.<sup>1</sup>

## CONCLUSIONS

The interaction of epoxy adhesive components with different forms of alumina has been modeled using molecular dynamics simulation techniques. The method facilitates visualization of preferred orientations of organic molecules with respect to alumina surfaces, and suggests which functional groups are critical in determining these orientations. The model also evaluates the relative affinities of organic species for the alumina surfaces and determines to what extent critical bond lengths in the organic molecules are affected by proximity to the surfaces. The calculated results can be qualitatively correlated to experimental observations of the effects of alumina on the reactivity of epoxy adhesive monomers. The results illustrate how simulations could potentially be used to aid the design of improved adhesives. The results of the simulations have already been useful in suggesting future areas of research.

Figure 1. Model surface of corundum.



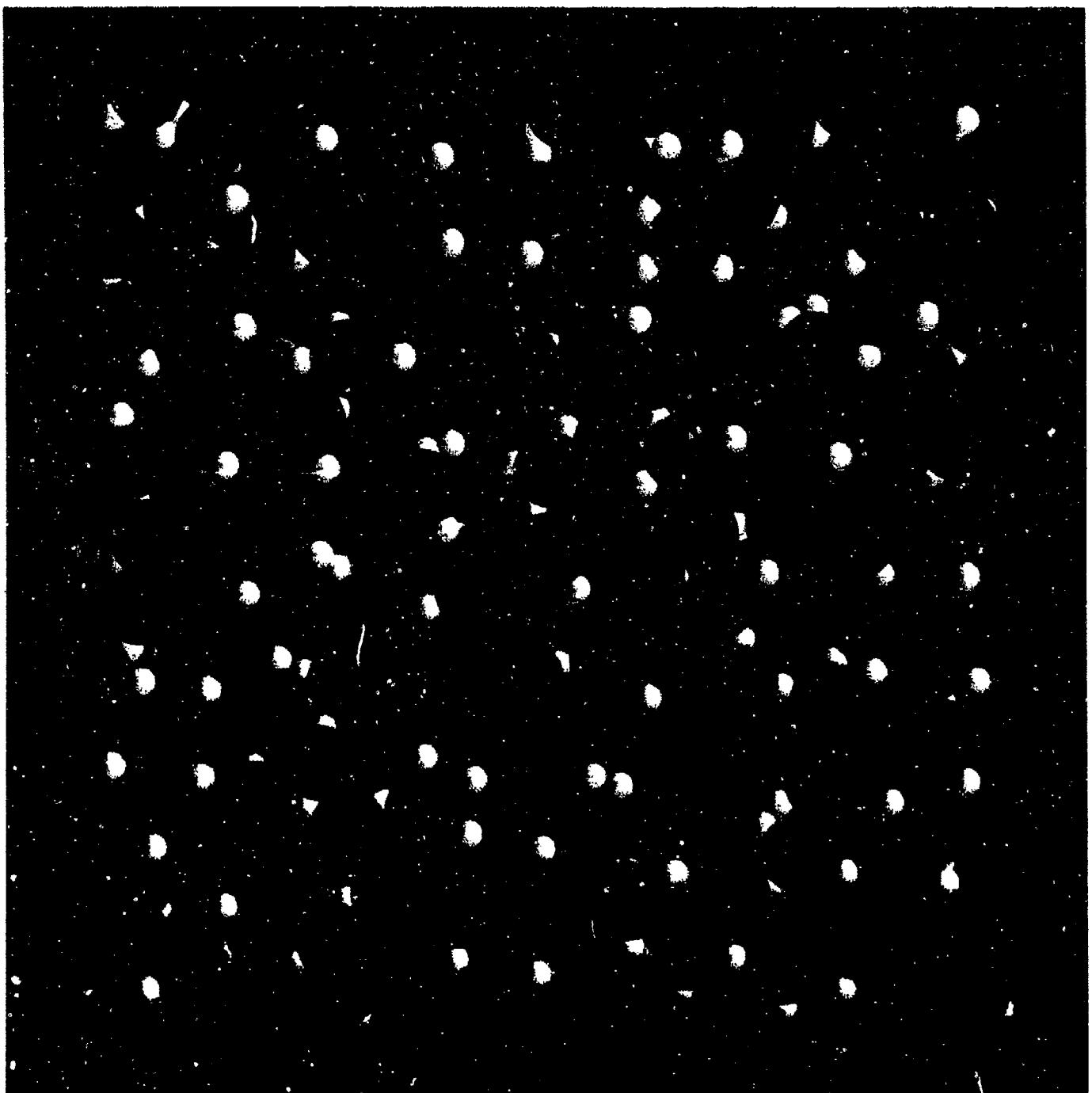


Figure 2 Model surface of amorphous alumina

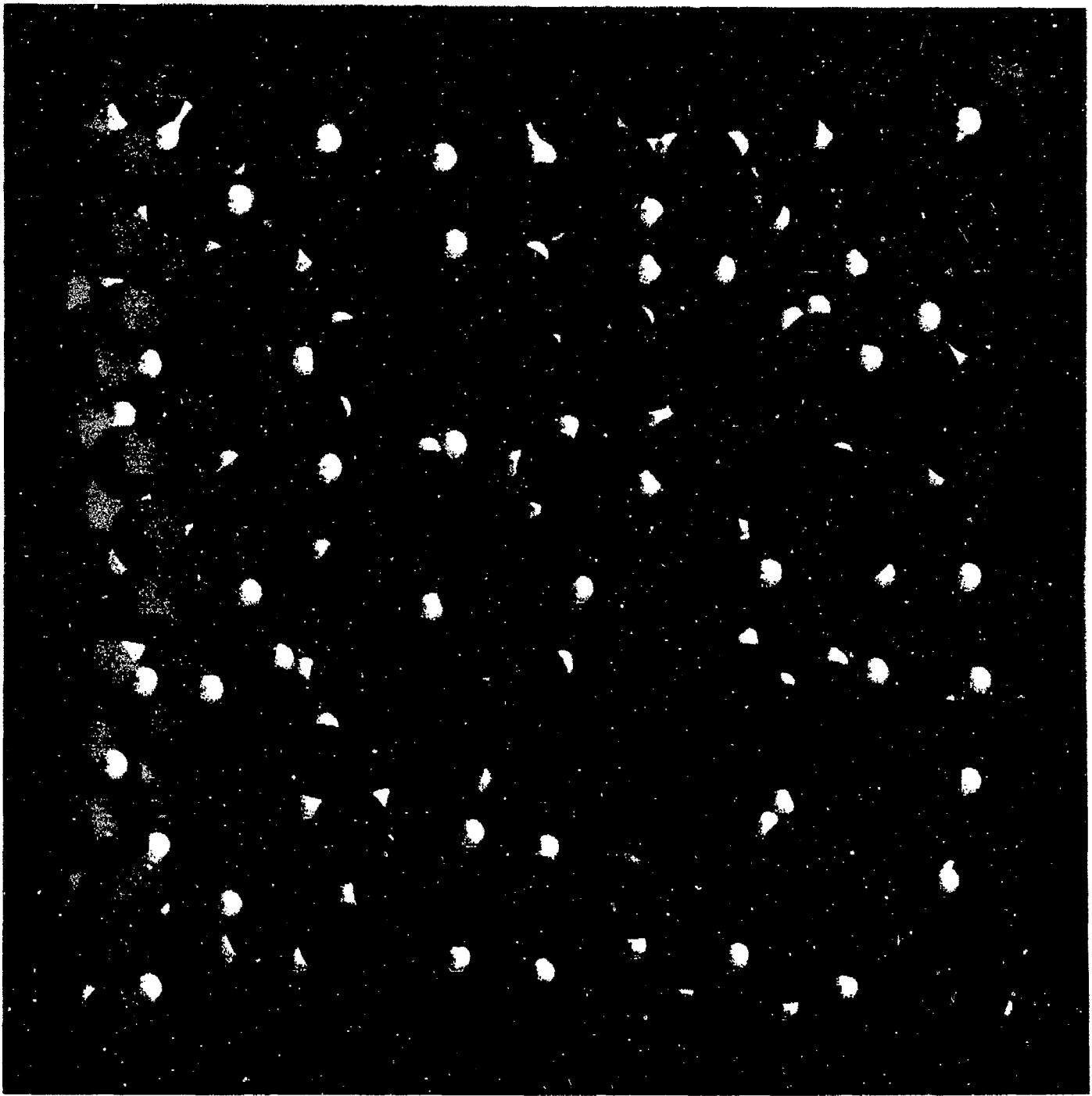


Figure 3. Moxide surface of amorphous alumina with 3 wt % adsorbed water

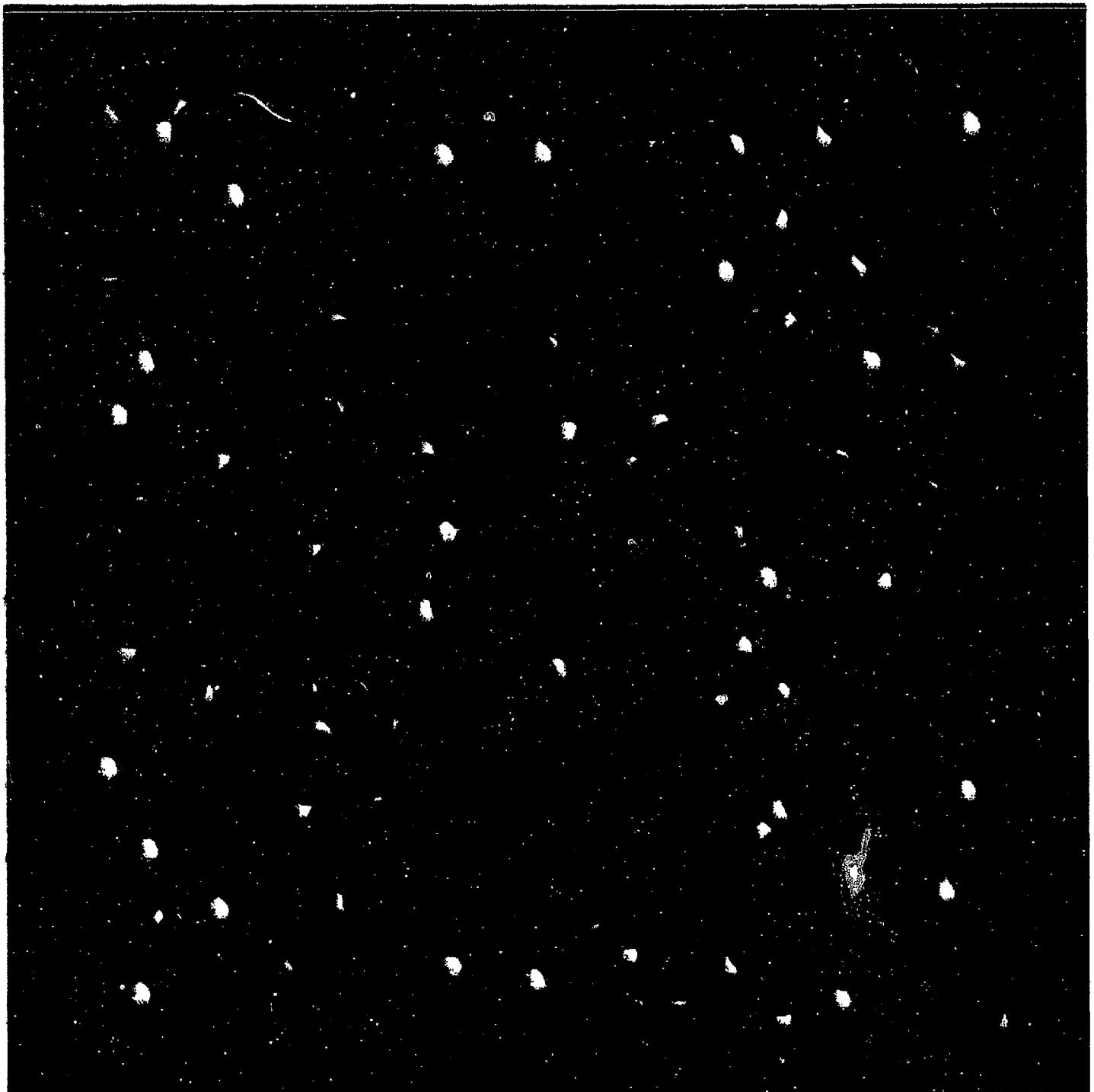


Figure 4. Model surface of amorphous alumina with 7.5 wt.% adsorbed water.

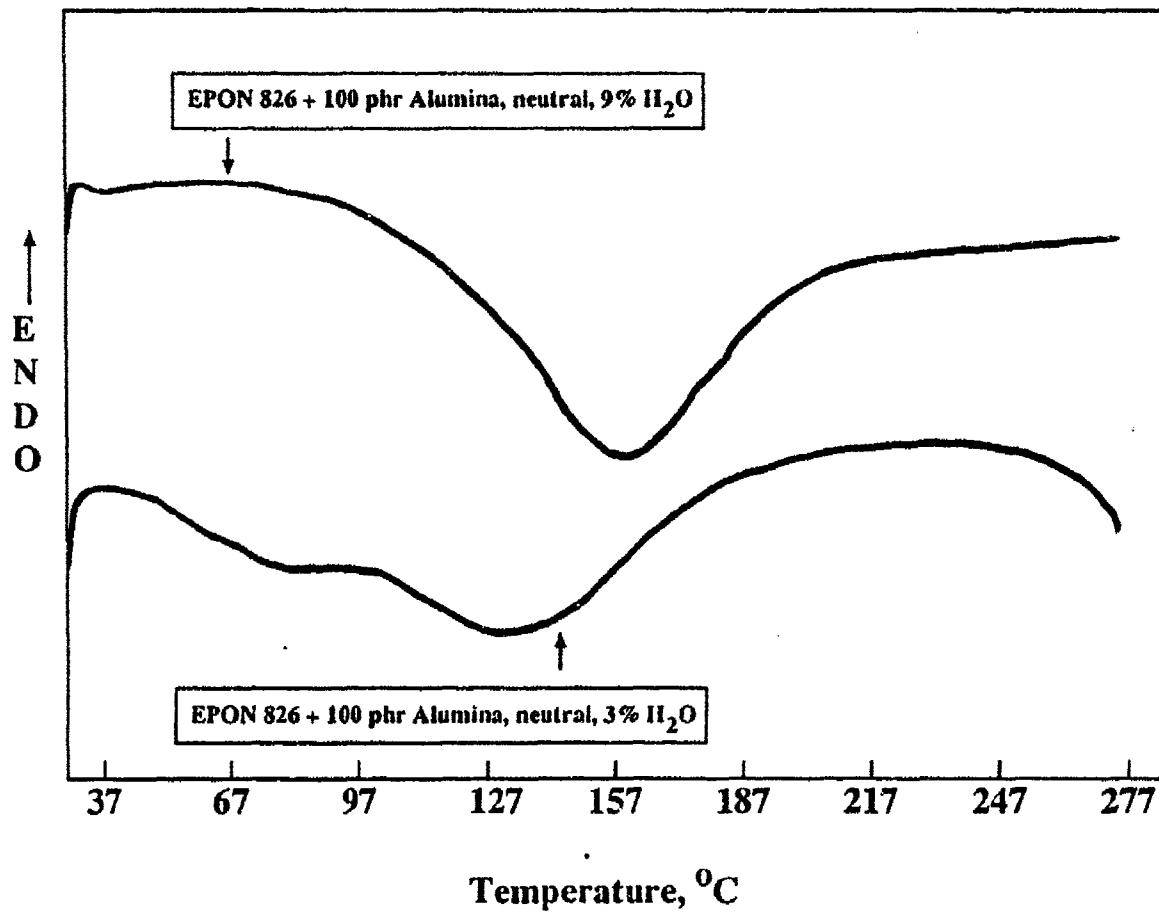


Figure 5. Effect of water addition on epoxy homopolymerization  
in the presence of alumina, dynamic DSC, 10°C/min.

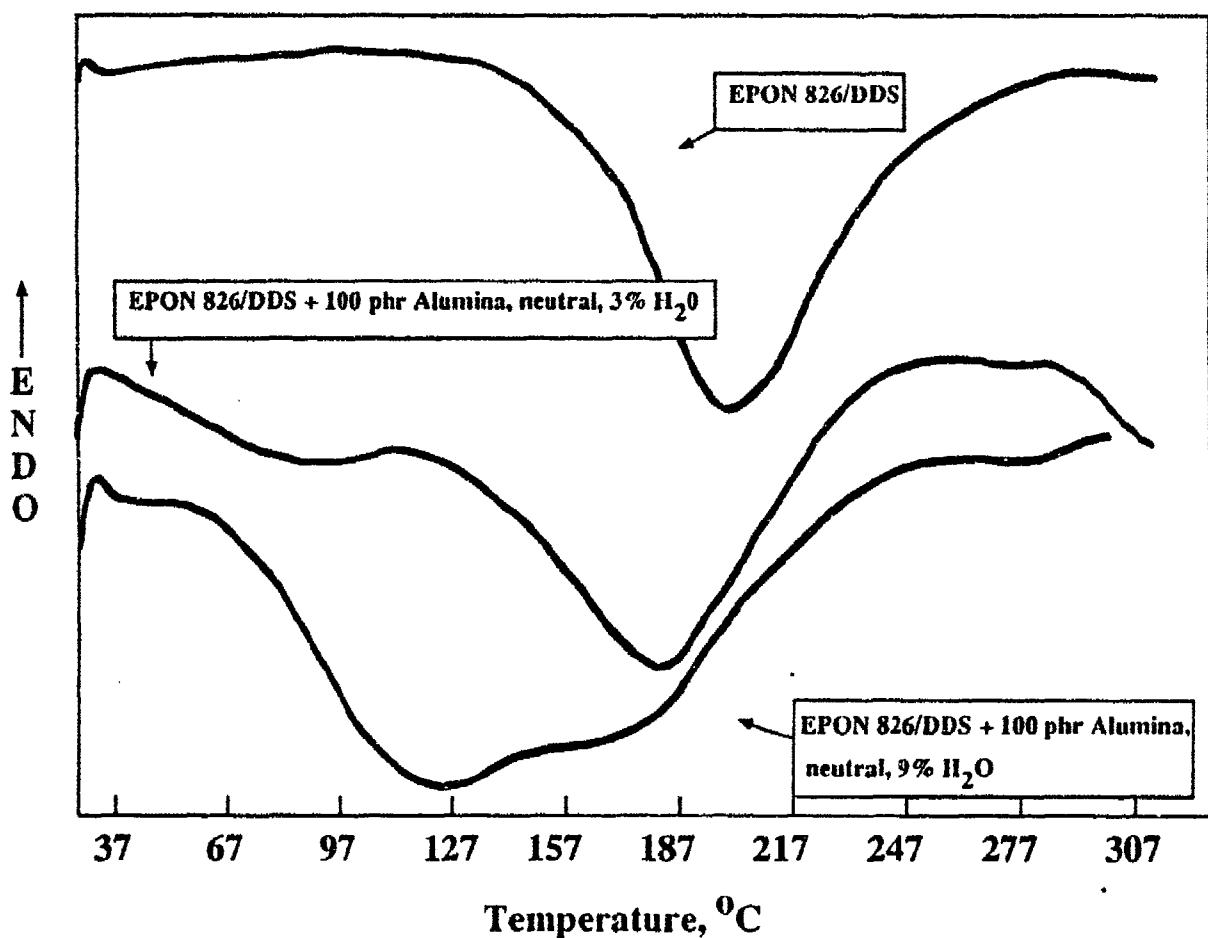
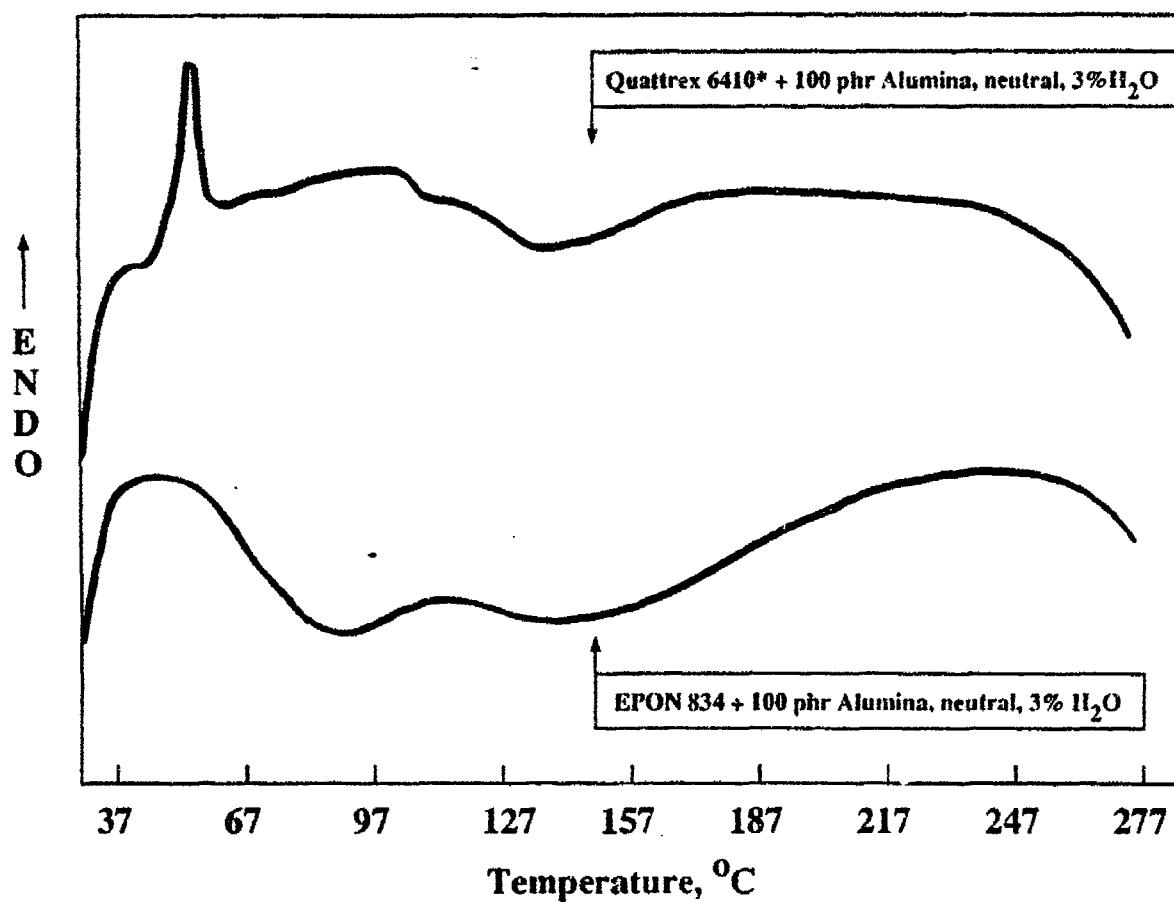


Figure 6. Effect of water addition on epoxy-amine reactions  
in the presence of alumina, dynamic DSC, 10°C/min.



\*Quattrex 6410 = epoxy resin based on DGEBA-Br

Figure 7. DSC comparison of DGEBA and DGEBA-Br reactivity  
in the presence of alumina, dynamic DSC, 10°C/min.

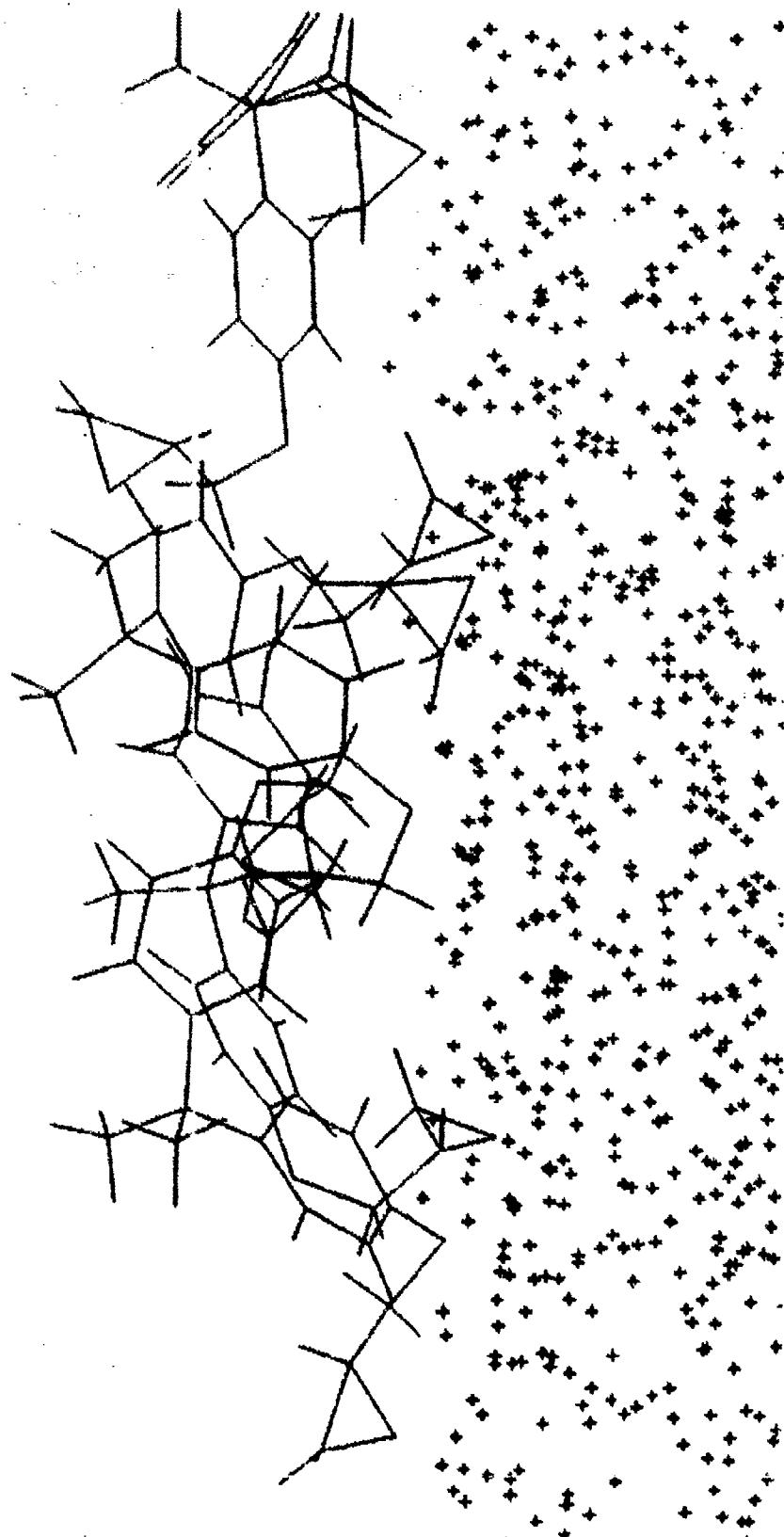


Figure 8. Simulation of DGEBBA on amorphous alumina.

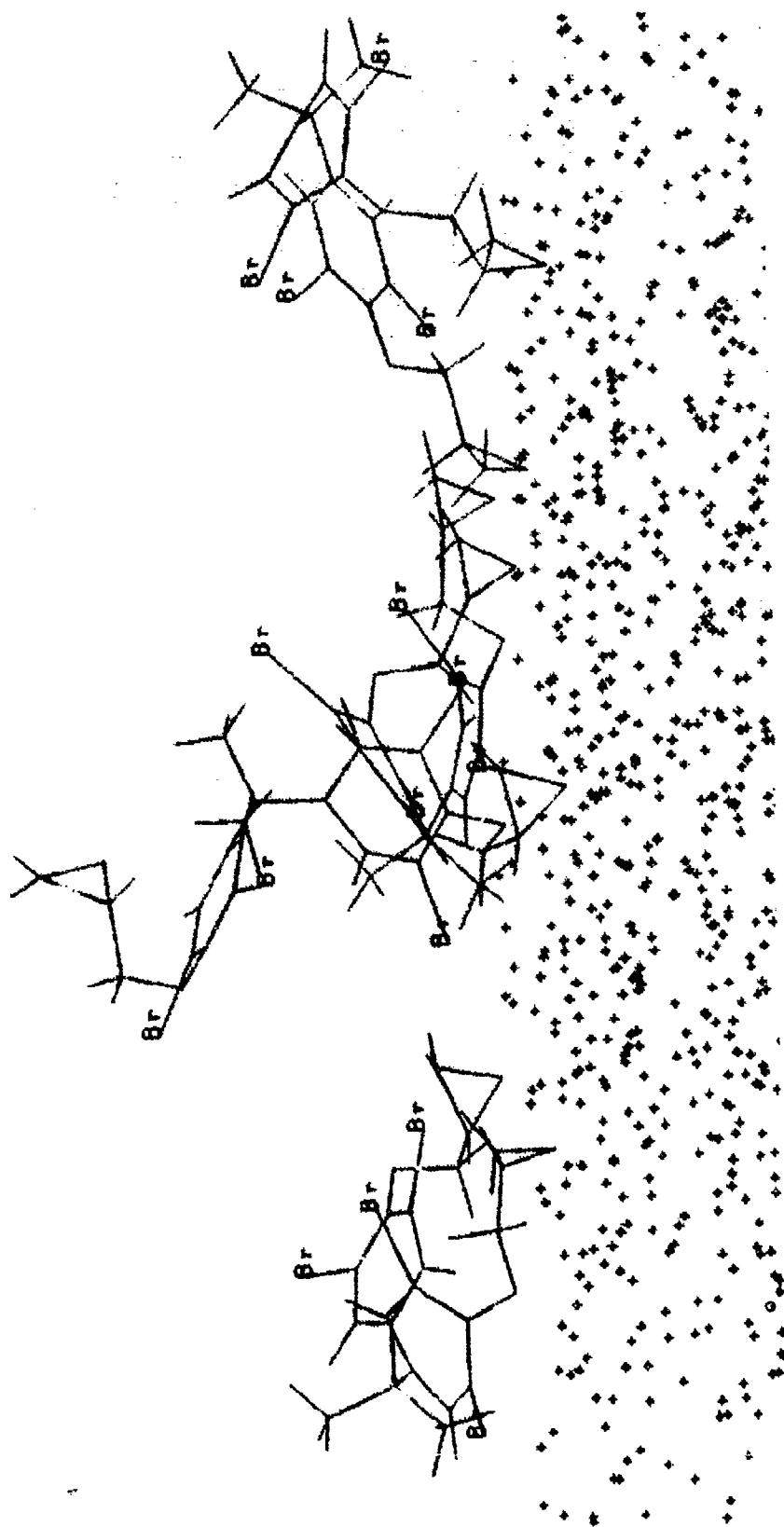


Figure 9. Simulation of DGEBA-Br on amorphous alumina.

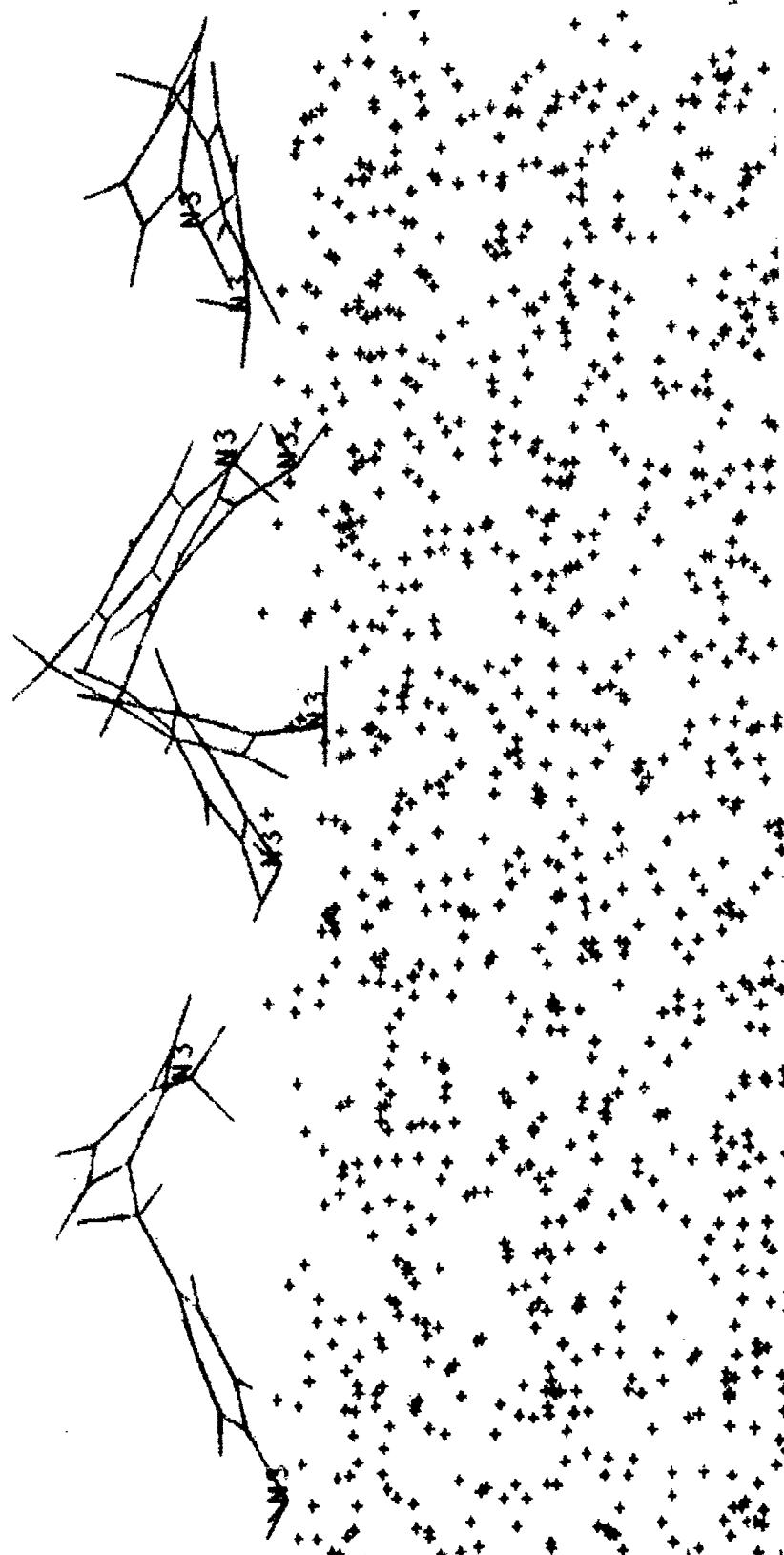


Figure 10. Simulation of MDA on amorphous alumina.

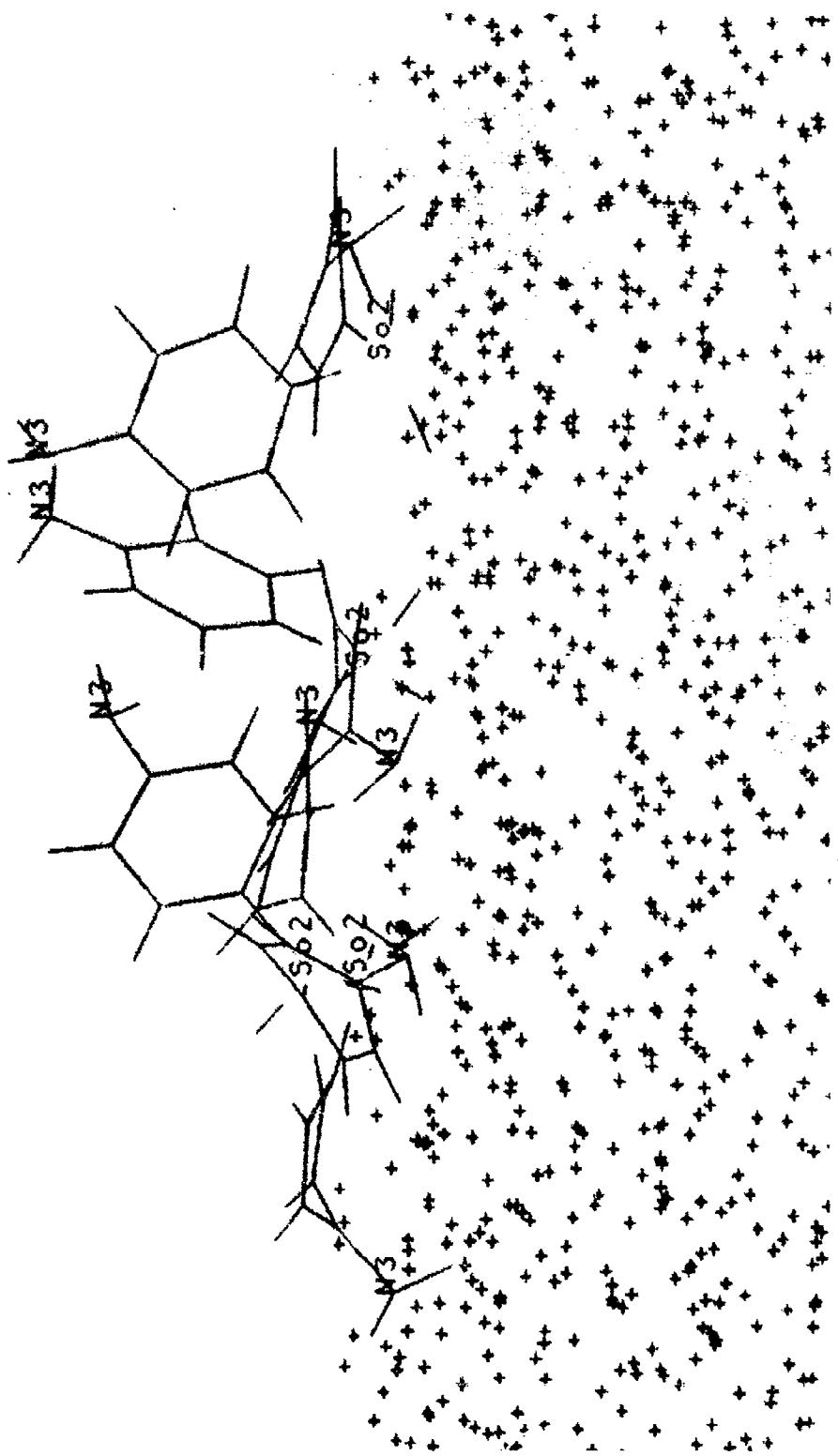


Figure 11. Simulation of DDS on amorphous alumina.

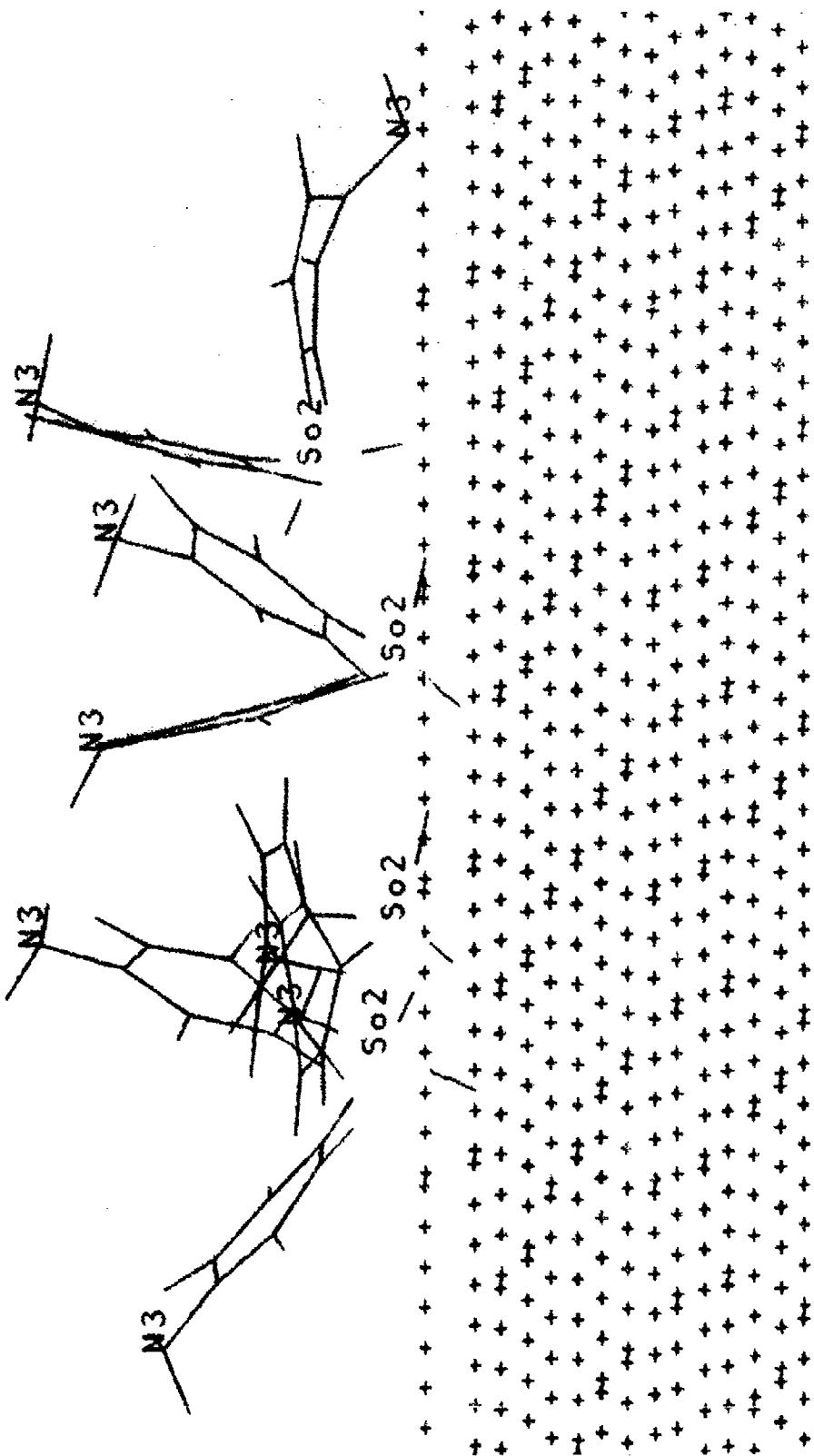


Figure 12. Simulation of DDS on corundum.

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U.S. Army Materials Technology Laboratory  
Watertown, Massachusetts 02172-0001  
COMPUTER SIMULATIONS OF EPOXY ADHESIVE  
MONOMER INTERACTIONS WITH ALUMINA SURFACES -  
Michael S. Sennett, Walter X. Zukas, and Stanley E. Wentworth

Technical Report MTL TR 92-54, August 1992, 28 pp -  
Illus-tables

An ongoing program in our laboratory seeks to elucidate the effect of aluminum oxide on the cure chemistry of epoxy adhesives. The project includes the use of molecular dynamics (MD) techniques to carry out real time simulations of the interaction of various epoxy adhesive monomers with idealized alumina surfaces. Adhesive monomers investigated include the diglycidyl ether of bisphenol A (DGEBA), a brominated form of DGEBA, diaminodiphenyl sulfone (DDS) and methylene dianiline (MDA). Both crystalline and amorphous forms of alumina at different levels of hydration have been simulated. The simulations illustrate the preferred orientations of the organic molecules with respect to the alumina surfaces and suggest which functional groups are most influential in determining this orientation. The model and experimental systems correlate well, showing similar response to changes in organic molecular structure, alumina morphology, and level of hydration. Model studies of this type can aid the understanding of the critical interphase region of adhesive bonds, including factors which affect bond durability, and have the potential to be used in the design of improved adhesives.

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